

Improved Synthesis of Polyether-Aramid Multi-Block Copolymers by Direct Polycondensation

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(Received April 25, 1985)

ABSTRACT: Polyether-aramid multi-block copolymers having structural regularity were synthesized by a one-pot two-step method of direct polycondensation using triphenyl phosphite and pyridine as condensing agents. Amine-terminated telechelic aramid oligomers were prepared by the reaction of bis(4-aminophenyl) ether and isophthalic acid, and subsequently condensed with α,ω -poly(oxyethylene)dicarboxylic acid giving the multi-block copolymers with inherent viscosities of 0.5—0.7 dl g⁻¹. No appreciable differences in thermal and tensile properties were observed between the multi-block copolymers thus prepared and those synthesized by the previously reported two-pot method. In contrast, the properties of these block copolymers differed significantly from those of a randomly coupled block copolymers prepared by the one-step procedure.

KEY WORDS Polyether-Aramid Multi-Block Copolymers / Direct Polycondensation / Solubility / Thermal Behavior / Tensile Properties /

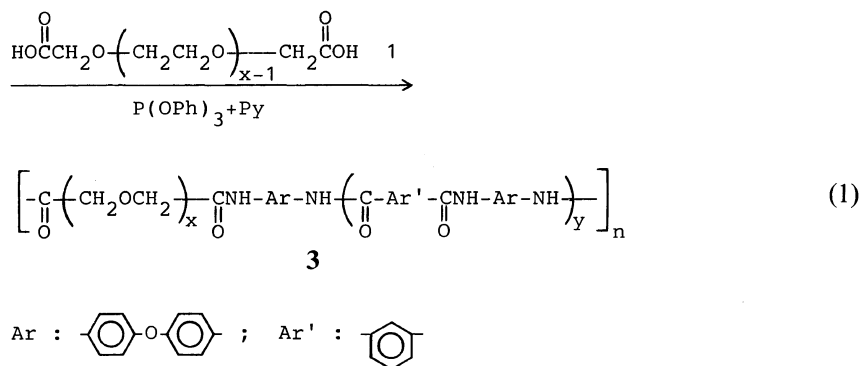
In our previous paper¹ dealing with the synthesis of multi-block copolymers based on poly(oxyethylene)s and aromatic polyamides (aramids), it was reported that polyether-aramid multi-block copolymers can be obtained by the direct polycondensation of amine-terminated telechelic aramid oligomers (aramid diamines) with α,ω -poly(oxyethylene)dicarboxylic acids (POE-diacids) using triphenyl phosphite and pyridine as condensing agents. This synthetic procedure, referred to as a two-pot method, is advantageous for the synthesis of the multi-block copolymers having high structural regularity but is somewhat troublesome because of the isolation of aramid diamines in the first stage. The present work was undertaken to observe whether an improved one-pot two-step method, which consists of *in situ* preparation of aramid diamines and subsequent poly-

condensation with POE-diacids in one-pot, could be worked out for synthesizing the multi-block copolymers with well-defined structures. The simplest one-step method, where parent aromatic diamine and dicarboxylic acid for aramid diamine, and POE-diacids are reacted together, was also investigated for comparison.

EXPERIMENTAL

Materials

POE-diacid (**1**) having a number average molecular weight of 3400, determined by titration, was supplied by Kawaken Fine Chemicals Corp. Bis(4-aminophenyl)ether (ODA) and isophthalic acid (IPA) were purified by recrystallization from tetrahydrofuran and aqueous ethanol, respectively. Triphenyl phosphite, pyridine, *N*-methyl-2-



The synthesis of multi-block copolymers **3(I/II)** was performed by the one-pot two-step method. The reaction of IPA with calculated excess of ODA in the presence of triphenyl phosphite and pyridine in NMP afforded a solution of aramid diamine **2**, which in turn was subjected to polycondensation with POE-diacid **1** giving multi-block copolymers **3(I/II)**. The calculated amounts of IPA and ODA were used to form aramid diamines having a desired number average molecular weight (M_n), and exactly the equal molar amount of POE-diacid **1** was used to the amount of aramid diamine **2** prepared *in situ*. From combinations of POE-diacid **1** and four aramid diamines **2a—2d** with M_n ranging from 1200 to 5500, multi-block copolymers **3a(I/II)—3d(I/II)** were obtained in high molecular weights as suggested by their high inherent viscosities (0.5—0.7 dl g⁻¹).

The simplest one-step method was applied to the preparation of block copolymers **3(I)**. Three reaction components, ODA and IPA for aramid diamine, and POE-diacid, were reacted together in NMP using triphenyl phosphite and pyridine as the condensing agents. Block copolymers **3(I)** having inherent viscosities of 0.6—0.9 dl g⁻¹ were obtained in almost quantitative yields.

The results of the synthesis of block copolymers of **3(I/II)** and **3(I)** series, as well as previously reported block copolymers **3(II)** by the two-pot method,¹ are summarized in Table I. The inherent viscosity values of **3(I/II)** were

Table I. Synthesis of polyether-aramid multi-block copolymers

Method of preparation ^a	M_n of aramid oligomer	Block copolymer	
		Code	η_{inh}^b dl g ⁻¹
II	2000	3b(II)	0.64
II	3300	3c(II)	0.65
II	5400	3d(II)	0.52
I/II	1200	3a(I/II)	0.50
I/II	1900	3b(I/II)	0.69
I/II	3200	3c(I/II)	0.51
I/II	5500	3d(I/II)	0.57
I	1200	3a(I)	0.67
I	1900	3b(I)	0.75
I	3200	3c(I)	0.71
I	5500	3d(I)	0.93

^a II, two-pot method; I/II, one-pot two-step method; and I, one-step method.

^b Measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C.

Table II. Elemental analysis of polyether-aramid multi-block copolymers

Block copolymer	Calcd/%			Found/%		
	C	H	N	C	H	N
3c(II)	63.40	6.65	4.35	61.76	6.57	3.88
3c(I/II)	—	—	—	61.75	6.40	4.43
3c(I)	—	—	—	62.57	6.45	4.41
3d(II)	65.63	6.08	5.33	64.17	5.85	4.80
3d(I/II)	—	—	—	65.48	5.87	5.47
3d(I)	—	—	—	66.33	5.87	5.32

almost the same as those of **3(II)**, whereas the values of **3(I)** were comparatively higher than those of **3(I/II)** and **3(II)**.

The structure of the resulting polymers was confirmed by IR spectroscopy and elemental analysis (Table II). The IR spectra of all the block copolymers **3(I/II)** and **3(I)** were almost identical with those of multi-block copolymers **3(II)**.¹ In the IR spectra of both **3(I/II)** and **3(I)**, characteristic amide absorptions at 3300 cm^{-1} (N-H) and 1660 cm^{-1} (C=O), and ether absorptions at 1225 and 1100 cm^{-1} appeared, while a strong carbonyl absorption at 1740 cm^{-1} due to the carboxylic function of the starting POE-diacid disappeared.

Properties of Polyether-Aramid Multi-block Copolymers

Both block copolymers of **3(I/II)** and **3(I)** are readily soluble in DMAc, but insoluble in other organic solvents including NMP, pyridine, *m*-cresol, and formic acid. The difference in solubility between **3(I/II)** and **3(I)** was not observed clearly. Furthermore, the solubility behavior of these block copolymers was the same as that of multi-block copolymers **3(II)**.¹

Transparent, ductile, and elastomeric films could be cast from the DMAc solutions of all the block copolymers. From small-angle X-ray diffraction studies of the films, a diffraction peak was observed at a diffraction angle of 10.6, 12.0, and 11.2 min, for polymer films **3c(II)**, **3c(I/II)**, and **3c(I)**, respectively. The average interdomain distance for **3c(II)**, **3c(I/II)**, and **3c(I)** was calculated to be 25, 22, and 24 nm, respectively, from known Bragg's equation. The above results suggest that all of these transparent films have micro-phase separated structures.

In order to obtain more information about the microstructure of films of block copolymers, the films were examined by transmission electron microscopy using osmium tetroxide or ruthenium tetroxide as a staining agent.² However, attempts to prepare the

Table III. Glass transition temperatures (T_g) of poly(oxyethylene) segment in polymer-aramid multi-block copolymers

Block copolymer	POE content wt%	$T_g^a/^\circ\text{C}$		
		(II) series	(I/II) series	(I) series
3a	74	—	-39	-27
3b	63	-36	-33	-28
3c	51	-34	-36	-28
3d	39	-33	-31	-30
POE ^b	100	-38	-38	-38

^a Determined by DSC at a heating rate of $20^\circ\text{C min}^{-1}$ in air.

^b Poly(oxyethylene) homopolymer ($M_n=20000$).

micrographs having high image contrast were unsuccessful.

Two-phase polymers that segregate into distinct large domains usually exhibit two glass transition temperatures (T_g s) identical with those of the component polymers. When the domains are very small, the T_g s of the individual components shift; elevation of the temperature of the low T_g and depression of the high T_g . This inward-shift phenomenon has been reported for many block copolymers.³ The T_g s of multi-block copolymers **3(II)**, **3(I/II)**, and **3(I)** were evaluated by means of DSC. The high T_g s based on the aramid phase in the block copolymers could not be detected in the 250°C region because of the appearance of a strong exothermic peak due to decomposition of the poly(oxyethylene) (POE) phase, while the low T_g s based on the POE phase were detected clearly in the -30°C region. As can be seen from Table III, the T_g s of the POE phase remained almost unchanged over all the POE content, or tended to increase to some extent with decreasing POE content in the multi-block copolymers of the individual series.

No appreciable difference in the extent of T_g elevation was observed between block copolymers **3(II)** and **3(I/II)**, whereas the change of the T_g of block copolymers **3(I)** was rather

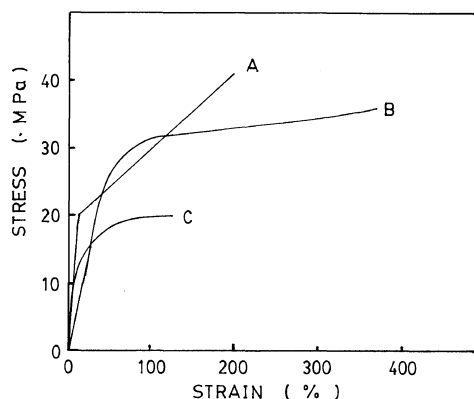


Figure 1. Stress-strain curves of films of polyether-aramid multi-block copolymer **3d(II)** (A), **3d(I/II)** (B), and **3d(I)** (C).

Table IV. Tensile properties of cast films of polyether-aramid multi-block copolymers

Block copolymer	Tensile strength	Elongation at break	Tensile modulus	Elastic recovery ^a
	MPa	%	MPa	%
3a(I/II)	4.9	320	8	76
3a(I)	2.8	280	8	53
3b(II)	6.9	370	6	100
3b(I/II)	7.0	860	6	88
3b(I)	3.2	350	5	66
3c(II)	29	320	470	86
3c(I/II)	26	290	240	79
3c(I)	11	280	440	81
3d(II)	42	200	500	58
3d(I/II)	36	360	300	53
3d(I)	20	140	700	49
Aramid ^b	68	4	1700	—

^a Measured by 100% extension of film specimens and relaxation.

^b Aramid homopolymer prepared by polycondensation of 4,4'-ODA and IPA. Inherent viscosity was 0.80 dl g⁻¹ measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C.

large as compared with block copolymers **3(II)** and **3(I/II)**. This fact may suggest that block copolymers **3(I/II)** have high structural regularity, very similar to multi-block copolymers **3(II)**,¹ while block copolymers **3(I)** are randomly coupled block copolymers having some irregular structures.

Stress-strain curves of the films of block copolymers **3(II)**, **3(I/II)**, and **3(I)** were obtained by a tensile tester. Typical curves are shown in Figure 1, and the tensile properties are summarized in Table IV. The films have ductile and elastomeric properties depending markedly on the content of aramid blocks which acts as pseudo-crosslinking sites. In general, tensile strength and modulus increased with increasing the aramid content, whereas elongation at break decreased. Similar structure-property relationships have been reported in polybutadiene-aramid multi-block copolymers.^{4,5}

The influence of the molecular structures of the block copolymers, mainly depending on the methods of polymer synthesis, was further observed on the tensile properties. Although the films of block copolymers **3(I/II)** have somewhat lower tensile strength and higher elongation at break than those of multi-block copolymers **3(II)** with well-defined structures, the difference in the tensile values is rather small between these two block copolymers. But both the tensile strength and elongation at break for the films of block copolymers **3(I)** are less than those of block copolymers **3(I/II)** and **3(II)**. This suggests that block copolymers **3(I)** have some irregularly coupled structures, compared with block copolymers **3(I/II)** as well as multi-block copolymers **3(II)** having high structural regularity. It is, therefore, concluded that the synthesis of polyether-aramid multi-block copolymers, whose structures are very similar to those of multi-block copolymers **3(II)** prepared by the troublesome two-pot procedure, were greatly improved through the simple one-pot two-step method.

Acknowledgment. We are indebted to Mr. T. Katsuta of Japan Synthetic Rubber Co., Tokyo, for preparing the electron micrographs, to Dr. H. Ikeda of the same company for the thermal measurements, and to Professor K. Miyasaka for the X-ray diffraction studies and for the tensile property de-

terminations. We also thank Professor T. Inoue for helpful comments.

REFERENCES

1. Y. Imai, M. Kajiyama, S. Ogata, and M. Kakimoto, *Polym. J.*, **16**, 267 (1984).
2. M. Kita, H. Tanaka, and T. Shimada, *Sen-i Gakkaishi*, **40**, T-411 (1984).
3. T. Inoue, S. Ogata, M. Kakimoto, and Y. Imai, *Macromolecules*, **17**, 1417 (1984).
4. S. Ogata, M. Kakimoto, and Y. Imai, *Macromolecules*, **18**, 851 (1985).
5. S. Ogata, H. Maeda, M. Kakimoto, and Y. Imai, *Polym. J.*, **17**, 935 (1985).